

ACTIVATION OF CARBON DIOXIDE AS AN OXIDANT OVER ZSM-5 ZEOLITE-SUPPORTED METAL OXIDE CATALYSTS

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INTRODUCTION

Chemical fixation of carbon dioxide has been concentrated on the conversion of CO_2 with various kinds of reductants into the usable chemicals in mass(1). These are mainly based on the reduction of CO_2 . As a different way, CO_2 can be considered as an oxidant. Bartholomew(2) reported that oxidizability in the gasification of coke was the following order: $\text{O}_2[105] > \text{H}_2\text{O}[3] > \text{CO}_2[1] > \text{H}_2[0.003]$, which numbers in parenthesis indicated the relative ratios of the gasification with oxidants. CO_2 has been called as nontraditional, unusual or mild oxidant and oxygen transfer agent. In this sense, carbon dioxide could be proposed as an oxidant in the oxidative conversions of hydrocarbons.

There have been some examples of utilization of carbon dioxide as an oxidant(3-5). Krylov and Mamedov(3) have studied on the oxidative conversions of alkanes, alkenes, and alcohols with carbon dioxide over Mn oxide-based catalysts and reported that oxygen generated during CO_2 reduction might participate in both partial oxidation and dehydrogenation. Yoo *et al.*(4) showed that Fe/Mo/borosilicate catalyst could activate CO_2 which could be functioning as a promoter and co-oxidant for the gas-phase oxidation of alkylaromatics with oxygen as well. Sugino *et al.*(5) reported that considerable increase in the conversion of ethylbenzene was observed with an iron-loaded catalyst in the presence of carbon dioxide, which revealed that the reaction proceeded via an oxidative dehydrogenation mechanism by CO_2 .

Even though ZSM-5 zeolite has favorable adsorption property for various gases, micropore structure, high surface area, and highest thermal stability among zeolites, it has been rarely applied for supporting metal oxides. However, recently a few trials for utilizing ZSM-5 zeolite as a support for metal oxides have been appeared(6). In our previous study, it was shown that ZSM-5 zeolite could play an important role as a support for the reduced KNiCa oxide in CO_2 reforming of methane(7).

Ferrite-type oxides are known as materials exhibiting ferri- or ferromagnetism as spinel oxides and oxygen deficiency in structure(8). However, catalytic application of these ferromagnetic oxides are not so much. As an example of catalyst, ferrite was reported to be active for the selective oxidative dehydrogenation of hydrocarbons(9). Recently, it was shown that oxygen-deficient ferrites or magnetite was very reactive in the decomposition of CO_2 to carbon at 300°C (10).

In this study, the oxidative transformation of hydrocarbons such as propane and ethylbenzene was investigated by using CO_2 as an oxidant over zeolite-supported spinel oxide catalysts such as ferrites or magnetite having oxygen deficiency.

EXPERIMENTAL

Zeolite-supported magnetite ($\text{Fe}_3\text{O}_{4.8}$) and metal-containing ferrites ($\text{MFe}_2\text{O}_{4.8}$, $\text{M} = \text{Ni}^{2+}$, Mg^{2+}) were prepared by air oxidation of aqueous suspensions of Fe(II) and M(II) mixed hydroxides in slightly alkaline solution(11). These catalysts were dried *in vacuo* at 80°C and calcined under N_2 flow at 400°C for 3h. Zeolites used as supports were NaZSM-5 (Zeocat PZ-2, $\text{Si/Al} = 980$) and NaY (Zeocat Z6-01-01, $\text{Si/Al} = 2.4$). Loading of metal oxide on all the catalysts was 1.5 or 5.0 wt.%. Zeolite-supported KNiCa oxide (0.8 wt.% K-5 wt.% Ni-12 wt.% Ca), prepared by the solid-reaction method(7), was tested in the propane conversion for comparison.

All the catalytic measurements were carried out in a fixed-bed quartz reactor (i.d., 10 mm) at atmospheric pressure. In the case of oxidative dehydrogenation of ethylbenzene with CO_2 , the reaction was performed by feeding ethylbenzene into the reactor by passing CO_2 through the ethylbenzene saturator thermostated at 25°C . The condensed effluent was analyzed by FID-GC. And effluent gases were analyzed by on-lined TCD-GC. The propane conversion with CO_2 were carried out at 800°C . The reactant gas mixture consisted of carbon dioxide and propane ($\text{CO}_2/\text{C}_3\text{H}_8 = 3$) diluted with nitrogen was co-fed into the reactor. The gaseous compositions of reactants and products were analyzed by on-lined TCD-GC.

RESULTS AND DISCUSSION

Reactions of propane with carbon dioxide

Four types of reactions could be occurring during propane conversion with CO_2 . Each of them to a different extent on different catalysis; propane dehydrogenation by CO_2 into propylene, selective decomposition into ethylene, non-selective decomposition into methane, and deep conversion into CO and H_2 , so-called reforming. The conversion of propane with carbon dioxide over zeolite-supported metal oxide catalysts was found to be conducted in an oxidative manner by looking at the products such as propylene, ethylene, methane, and CO with H_2 and water (as shown in Table 1). Two-types of activity patterns depending on the catalysts were obtained. One was catalyst system giving the oxidative dehydrogenation activity which produced olefins such as propylene and ethylene. The other was the reforming activity which produced syngas together with methane.

Even though magnetite and ferrites catalysts produced carbon directly from carbon dioxide(8), zeolite-supported catalysts were found to be effective not only for the propane dehydrogenation into olefins, but also for CO_2 activation into CO. These activities were very much dependent on metallic components in spinel oxide as well as their loadings. For example, 1.5 wt.% $\text{NiFe}_2\text{O}_{4.8}/\text{ZSM-5}$ showed higher conversions of propane and CO_2 than those of 1.5 wt.% $\text{Fe}_3\text{O}_{4.8}/\text{ZSM-5}$ due to the high activity on the reforming of propane and non-selective CH_4 production instead of the oxidative dehydrogenation activity on ferrite-loaded catalyst. The activities of ZSM-5-supported spinel oxides such as magnetite and ferrite were strong in the formation of olefins comparing with the reduced $\text{KNiCa}/\text{ZSM-5}$, which was known as a good catalyst in the formation of syngas(6). This result indicated that active sites for the oxidative conversion into olefins and the reforming seemed to be different. It suggested that an active site of spinel supported catalysts was not metallic Ni, but rather oxygen defects or oxygen deficiency. Higher loading of ferrite oxides resulted in the increased propane conversion with the decreased propylene selectivity and large increase in ethylene selectivity, and attributed to rather decrease in the CO_2 conversion. In propane conversion with CO_2 , carbon dioxide was considered to be dissociatively cleaved on the oxygen-deficient sites into carbon monoxide and surface oxygen species, which could be functioning as an oxidant for the conversion of propane into olefins and syngas in an oxidative manner.

Effect of CO_2 in the dehydrogenation of ethylbenzene

The results of catalytic activities in the dehydrogenation of ethylbenzene with supported ferrite catalysts are shown in Table 2. The catalysts were used after reduction at 500°C for 1h, prior to using in the reaction. Specific activity in Table 2 indicates moles of styrene produced per mole of metal oxide in an hour. The dehydrogenation of ethylbenzene with CO_2 over hydrogen-treated ferrite catalysts produced styrene and hydrogen. Considerable activities for the reaction were observed with zeolite-supported ferrite catalysts. When the reaction was conducted under an excess of CO_2 stream, higher catalytic activity over $\text{NiFe}_2\text{O}_{4.8}/\text{ZSM-5}$ was obtained than in the case of a N_2 stream. Moreover, the dehydrogenation reaction over the catalyst using a N_2 stream exhibited considerable carbon deposition on the catalyst as compared to using a CO_2 stream. In addition, small amount of carbon monoxide during the reaction in a CO_2 stream was detected together with small amount of water. The zeolite-type as support had also influence on the activity in production of styrene. Comparing with dehydrogenation activity, ZSM-5 zeolite for supported ferrite catalysts appeared to be more suitable to support than Y zeolite. These results showed that zeolite-supported ferrite catalysts were to be active in the dehydrogenation of ethylbenzene to styrene and their activities were enhanced due to the presence of CO_2 . This indicated that the dehydrogenation reaction was enhanced by the oxidative manner due to the presence of CO_2 .

Evidence of oxygen deficiency by looking at the CO_2 dissociation

The activity of CO_2 decomposition into C over H_2 -treated ferrite or magnetite was found to be closely related with their oxygen deficiency(8). In order to confirm the role of oxygen deficiency of the supported spinel catalysts, the CO_2 dissociation into CO after reducing the catalysts with 5% H_2 at 500°C for 1h before putting into CO_2 pulse at 400°C . Supported-ferrite and magnetite catalysts showed significant activity of CO_2 dissociation even at lower temperature of 400°C , as presented in Table 3. In all cases, the amount of CO formed decreased greatly at initial stage and gradually at later stage with increase of the pulse numbers.

It was found that specific activities of CO formation over supported-ferrite or magnetite catalysts was much higher than those of unsupported nickel ferrite and reduced KNiCa/ZSM-5 as a reforming catalyst which was supposed to have a small oxygen deficiency. As above mentioned, the zeolite-type as support had also influence on the activity of CO formation. The activity of $\text{Fe}_3\text{O}_{4.8}/\text{ZSM-5}$ was almost two times higher than that of $\text{Fe}_3\text{O}_{4.8}/\text{Y}$ with same loading of $\text{Fe}_3\text{O}_{4.8}$. Moreover, the lower loadings of metal oxide gave the higher specific activities. It means that dispersion of oxygen deficient sites or oxygen defects was more efficient for the CO_2 dissociation.

It was known that ferrites and magnetite materials treated with H_2 at high temperature produced oxygen deficiency(12). It was considered that their ferromagnetism were partially related with their oxygen deficiency. In this sense, ferromagnetism of zeolite-supported ferrite or magnetite catalysts and CO_2 interaction with their ferromagnetism were examined by EPR (electron paramagnetic resonance) analysis. For example, very intensive FMR (ferromagnetic resonance) signal in EPR spectrum of 5 wt.% $\text{Fe}_3\text{O}_{4.8}/\text{ZSM-5}$ catalyst appeared only after evacuation at 500°C for 1h. This FMR signal gave a g value of 1.9 with $\Delta H_{pp} = 1140$ G (data not shown). After treatment with CO_2 at 600°C for 30 min, FMR intensities were significantly decreased. This supports that oxygen produced from CO_2 dissociation over the catalyst filled up the oxygen defect sites and resulted in the diminution of ferromagnetism.

In summary, not only oxygen from CO_2 molecule could be utilized as an oxidant but also surface design for chemisorptive CO_2 activation would be important in the heterogeneous activation of CO_2 as an oxidant. It was demonstrated that not only oxygen-deficient oxides such as ferrite and magnetite were active in the simultaneous activation of carbon dioxide and hydrocarbons, but also ZSM-5 zeolite could be suggested as a good support for the high dispersion of these spinels.

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Table 1. Conversion of Propane with CO₂ over Zeolite-Supported Metal Oxide Catalysts at 800°C^{a)}

Catalyst	Conversion, %		Yield, %		Olefin Yield, %	Olefin/CH ₄	CO/Olefin
	C ₃ H ₈	CO ₂	C ₃ H ₆	C ₂ H ₄			
1.5% Fe ₂ O ₄ /ZSM-5	66.1	18.5	31.0	15.1	46.1	2.77	1.7
5% Fe ₂ O ₄ /ZSM-5	97.3	8.7	7.7	41.0	48.7	0.23	0.9
1.5% NiFe ₂ O ₄ /ZSM-5	98.4	57.8	-	14.0	14.0	0.11	17.3
5% MgFe ₂ O ₄ /ZSM-5	94.0	21.8	6.0	36.5	42.5	0.30	2.0
KNiCa/ZSM-5 ^{b)}	68.2	91.6	4.8	-	4.8	0.05	38.2

^{a)} Reaction Condition : 800°C, P(C₃H₈) = 10 kPa, CO₂/C₃H₈ = 3, GHSV = 2 × 10⁴ h⁻¹.

^{b)} Same as Condition (a) except CO₂/C₃H₈ = 2; used in reaction after reduction 700°C for 1h.

Table 2. Dehydrogenation of Ethylbenzene with CO₂ over Zeolite-Supported Ferrite Catalysts at 600°C^{a)}

Catalyst	Styrene Yield (%)	Specific Activity ^{d)}
NiFe ₂ O _{4.8} /ZSM-5	38.3	100.8
NiFe ₂ O _{4.8} /ZSM-5 ^{b)}	33.9	89.2
NiFe ₂ O _{4.8} /Y ^{c)}	22.2	58.4
MgFe ₂ O _{4.8} /Y	19.2	43.3

^{a)} Loading of ferrites = 1.5 wt.%; W/F = 60 g-cat/h/mol; CO₂/EB = 30 : 1 (mol/mol); Catalyst pretreatment: reduction at 500°C for 1h. ^{b)} under N₂ flow without CO₂. ^{c)} reaction at 500°C.

^{d)} mol of styrene/metal oxide-mol h.

Table 3. The Dissociation of CO₂ over Zeolite-Supported Metal Oxide Catalysts at 400°C^{a)}

Catalyst	Amount of CO formed ^{b)} (μ mol)	Specific Activity ^{d)}
NiFe ₂ O _{4.8}	1.18	2.7
1.5% NiFe ₂ O _{4.8} /ZSM-5	0.75	117.2
1.5% Fe ₂ O _{4.8} /ZSM-5	0.46	70.9
5% Fe ₂ O _{4.8} /ZSM-5	0.62	28.7
5% MgFe ₂ O _{4.8} /ZSM-5	0.49	19.6
1.5% Fe ₂ O _{4.8} /Y	0.24	37.0
1.5% NiFe ₂ O _{4.8} /Y	0.22	34.4
KNiCa/ZSM-5 ^{b)}	1.63	19.1

^{a)} after reduction at 500°C for 1h. ^{b)} measured at 600°C after reduction at 700°C for 1h.

^{c)} One pulse contained 30.2 μ mol of CO₂. ^{d)} mmol of CO/mol of metal oxide.

^{e)} mmol of CO/ mol of metallic Ni.